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SLUDGE FORMATION IN SPR CAVERNS

FINAL TECHNICAL REPORT
Section 3

Origin, Composition and Physical Properties of Sludge-Entrained Brines

by
J. B. Green, S.K.-T. Yu, J.A. Green, J. W. Reynolds, D.A. Doughty and J. Y. Shay

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SLUDGE FORMATION IN SPR CAVERNS

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SECTION 3 - ORIGIN, COMPOSITION AND PHYSICAL PROPERTIES OF SLUDGE-ENTRAINED BRINES

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ABSTRACT

A number of crude oil storage caverns in the U.S. Strategic Petroleum Reserve (SPR) contain low levels (<0.3%) of a stable emulsion termed "sludge". In this work, the origin, composition and physical properties of brine entrained in sludge was investigated. Brine comprises anywhere from 5 to 50 percent of sludge, depending on the individual storage cavern and sampling depth. Sludge-entrained brine is derived from low concentrations of brine present in as-received crude oils, which ultimately settles out of the crude toward the bottom of the cavern. Thus, its composition largely reflects that of oilfield brine. In some caverns, fresh or brackish water used to displace crude oil in cavern operations has infused into the sludge layer, thereby diluting the brine in place. Organic constituents of brine include hydrophilic crude oil components, e.g. C_2-C_{20} carboxylic acids, as well as polyglycols used as demulsifying additives for oil/water separation in petroleum production. Total organic carbon of sludge brines is typically near 0.1 wt%. Brine is dispersed in sludge as droplets ranging in size from 30 down to <1 μm in diameter. The bulk of the brine can be removed from sludge via ultracentrifugation; the remaining noncentrifugable brine appears to be present in a highly dispersed, chemically stabilized state. Treatment of sludge with mineral acid or base often significantly affects the proportion of brine removable via ultracentrifugation. Based on this observation and others contained in the report, stabilization of brine in sludge occurs largely through chemical interactions rather than by simple physical entrapment.

INTRODUCTION

Earlier sections of the final report on sludge formation in the U.S. Strategic Petroleum Reserve (SPR)[1-3] dealt largely with two of the three major constituents of sludge - - crude oil and wax. This section focuses on the third component, brine. Many of the significant physical/chemical properties of sludge can be largely attributed to its brine component, e.g. its relatively high density, viscosity, acid neutralization number and, of course, salt content.

From a utilization standpoint, brine is by far the least desirable constituent of sludge. However, from the viewpoint of understanding the mechanism of sludge formation, sludge-entrained brine is quite valuable. As discussed in a preliminary report[4] and below, the composition of entrained-brine clearly points to settling as the major route to sludge formation. In addition, the discrete changes in brine content and composition observed with depth show sludge to exist in a highly stratified state - - with little intermixing between layers separated by distances as little as one foot.

After solution mining, the caverns used in SPR are full of saturated brine, which is drawn down as crude oil is put into place for storage. When the cavern is full, some of this original brine remains at the bottom of the cavern. In this report, brine left over from solution mining is referred to as "bulk brine", since it remains as a discrete phase or layer below the stored crude. Any sludge formed during crude oil storage occurs between the bulk crude and bulk brine phases. Interfacial distance is measured upward from the bulk brine/sludge interface, and is termed "Δ feet" (cavern depths are logged in feet).

The objectives of the work were to determine the origin, composition and physical properties of brine within the sludge layer (sludge-entrained brine). Since methodology and results from investigation of soluble organic constituents of entrained brine have been reported separately[5], only a brief summary of those findings will appear here.

EXPERIMENTAL

An Oympus Model BH-2 microscope was used for examining brine droplets in whole sludge samples prepared on standard microscope slides. Photomicrographs were taken of selected slides using various combinations of the filter and light polarization options available with the microscope.

The sludge samples themselves were obtained by lowering a 4L sample container into caverns at predetermined depths. Samples of bulk brine (brine in place below the stored crude) were taken similarly. Brine samples were isolated from sludge via ultracentrifugation at 40° C for one hour at a maximum relative centrifugal force (RCF) of 44,400.

Inorganic constituents were determined as follows. Water content was determined by Karl Fisher titration, NaCl content was usually calculated from ASTM D 4052 specific gravity, but in cases where only a small quantity of brine was available, it was determined gravimetrically. Bromide and sulfate contents were determined by ion chromatography using a Waters (Milford, MA) IC-Pak anion exchange column. A sodium borate/gluconate buffer and other experimental conditions recommended by Waters were employed in conjunction with a conductivity detector.

Other ions detectable with this method include fluoride, nitrite, nitrate and phosphate. These were not observed in any of the brines examined, including those pretreated with a silver-loaded adsorbent to reduce chloride interference in the detection of fluoride. Sr, V, Al, Cr, Fe, Pb and Mg concentrations were determined by flame atomic absorption. Stable isotope ratios were determined by Kruger Enterprises, Inc., Cambridge, MA. Total and organic carbon contents were determined by Huffman Laboratories, Golden, CO.

Acetic and propanoic acids were determined by gas chromatography (GC). A 30 m × 0.25 mm i.d., 0.25 μm film thickness Nukol bonded phase column (Supelco, Bellefonte, PA) was held at 185° C for the analysis. Flame ionization detector hydrogen and air flows were 30 and 400 mL/min, respectively; column flow was 1 mL/min He. To reduce analyte losses due to adsorption, oxalic acid was coinjected with each standard or sample. Thus, a 10 μL syringe was filled, in the following order, with: 1 μL air, 1 μL 1% oxalic acid, 1 μL air, and a known volume (usually 1-2 μL) of sample. Quantitation was by the method of external standards. Split injection (100:1) was employed; frequent changing of liners was required because of salt buildup. Analysis of other organic constituents was performed as described elsewhere.[5]

A series of NMR experiments was conducted to determine relaxation rates of sludge-entrained water. Initially the bulk of the sludge-entrained brine was removed via ultracentrifugation, and the water from the resulting brine was evaporated. A corresponding quantity of D_2O (99.8% D) was added to the brine residue to form reconstituted brine. This was in turn added back to centrifuged sludge, which was remixed at 85° C with vigorous shaking. The reconstituted sludge was then allowed to stand for a week, and recentrifuged. The resulting brine and centrifuged sludge was subsequently reblended in various proportions for measurements conducted using a JEOL GX270 NMR spectrometer at 41.47 MHz, ^2H frequency, using the inversion recovery method. Both linear and nonlinear methods were used to calculate the relaxation rate ($1/T_1$) as a function of temperature. The results were compared against those of pure D_2O and synthetic oil/water blends containing a known surfactant.

Another series of experiments was conducted to determine relative brine recovery from sludge via ultracentrifugation at various speeds. As part of this study, various additives were spiked into sludge to determine their effect on brine recovery as well. Thus, separate aliquots of neat or adulterated sludge were centrifuged at 17,000, 15,000, 13,000 and 11,000 rpm (RCF = 34,540, 26,890, 20,190 and 14,460 respectively). The quantity of separated brine was determined gravimetrically via its recovery using a syringe; the syringe needle was used to pierce the plastic centrifuge tube below the brine level and the brine was carefully drawn off.

RESULTS AND DISCUSSION

Microscopic Examination of Sludge

Figure 1 shows selected photomicrographs obtained during microscopic examination of sludge from a sweet crude cavern, West Hackberry (WH) 102 (see Section 1B[2]). This sludge was obtained 1 foot above the bulk brine/sludge interface and contained 10.6 wt% brine (sample no. 89SPR022). Figures 1a and 1b show different sections of the same microscope slide at 100× magnification; Figure 1c shows the same section as 1a at 200× magnification. Figure 1d shows a slide prepared from a centrifuged sample of the same sludge.

Figures 1a-1c illustrate the wide range in size of brine droplets (light circles) found in this sludge, which was typical of all other sludges examined. Droplets ranging from approximately 30 down to <1 μm may be discerned from close inspection of the figures. The presence of brine in submicroscopic particles, potentially in micellar systems, may be inferred from Figure 1d, which exhibits no visible droplets in spite of its approximately 3.5 wt% brine content. The visible particles in Figure 1d are clusters of microcrystalline wax.

An interesting feature of Figure 1b is the presence of several oil-encapsulated brine droplets (black circles), and a large (ca. 100 μm) clump of what appears to be oil, brine and possibly particulate matter (center of figure). The enrichment of sludge, relative to the parent crude, in high boiling acidic compounds was noted earlier in both Sections 1A and 1B of the final report on sludge formation.[1,2] The observed oil encapsulation of brine in Figure 1b may be visual evidence of this effect, thereby suggesting that coprecipitation with brine is the primary mechanism for the enrichment of sludge in high boiling acidic types.

The presence of microparticulate wax crystals is much more easily seen after removal of the bulk of the brine droplets via ultracentrifugation. However, the presence of wax crystals prior to centrifugation may be discerned from the grainy appearance of the background in the original photomicrographs of Figures 1a-1c (this was largely lost in their reproduction for this report). These microcrystalline waxes are responsible for the bimodal distributions of normal paraffins evident in gas chromatograms discussed earlier[3].

Overall, the photomicrographs in Figure 1 accurately depict sludge as a very heterogeneous material, which is consistent with its formation via settling of relatively dense materials insoluble in the bulk crude oil stored in the cavern. The local supersaturation of selected brine droplets with salt (e.g., elongated drop in Figure 1a (center) and partially shaded drop in Figure 1c) suggests compositional heterogeneity within the individual brine droplets, which is consistent with their relative isolation in the oil-based matrix. Similarly, the various degrees of brown shading observed for individual wax crystals in the photomicrographs (unfortunately, not easily seen in the
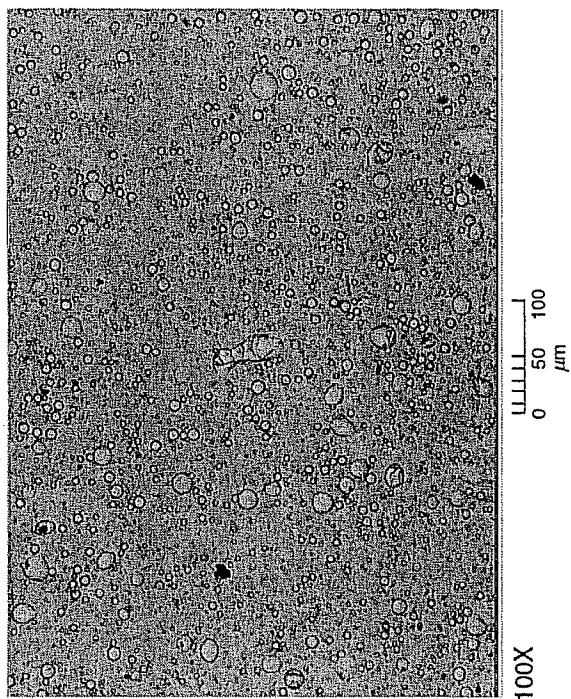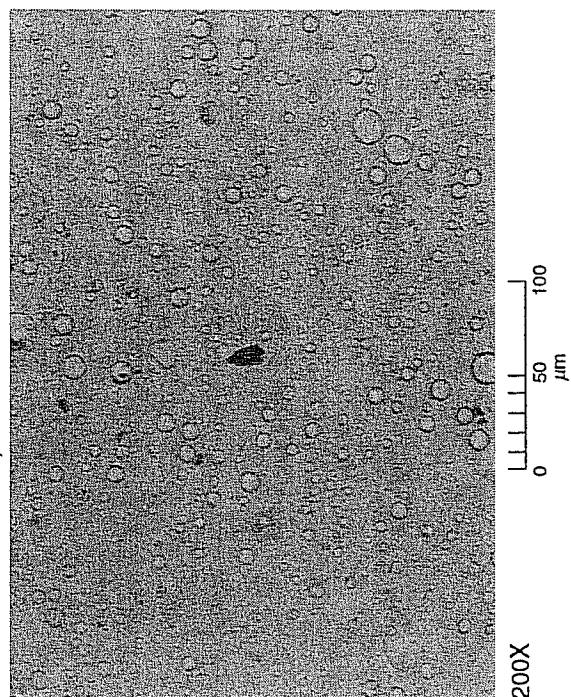
Figure 1. Photomicrographs of WH102 (Δfeet = 1) sludge. (a-c) are as-received sludges; (d) is sludge after ultracentrifugation.

reproduced figure) suggests a wide range of purity/composition for precipitated wax crystals as well.
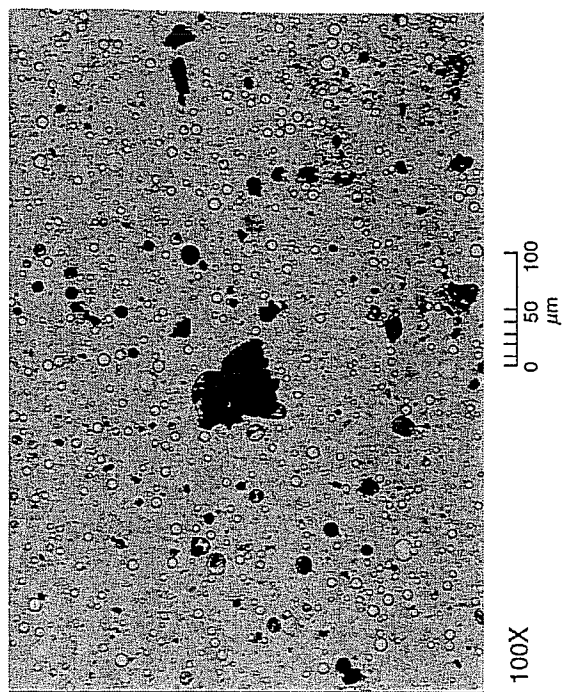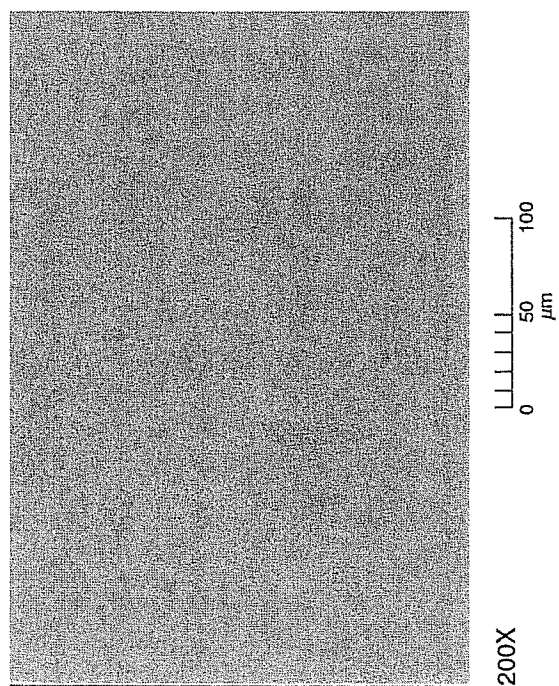
Figure 2 details some additional sludge features evident in microscopic examinations. Figures 2a and 2b compare brine droplet size distributions in centrifuged sludge from Bryan Mound (BM) Cavern 102 with (b) and without (a) addition of a 100 ppm spike of poly(ethylene glycol) (PEG). Various types of polyglycols are typically present in sludge-entrained brine.[5] In this case, the effects of added PEG were: (1) more uniform droplet size in brine remaining after centrifugation and (2) greater retention of brine after centrifugation. The water content of sludges shown in Figures 2a and 2b were 3.0 and 7.4 wt%, respectively.

Figure 2c shows mineral matter in a centrifuged sample of WH102 sludge. The significant sediment/ash content typical of sludge was discussed in Sections 1A and 1B[1,2]. Figure 2d shows a very unusual particle observed in the BM102 sludge. This relatively large (135 μm) "blob" is surrounded by a dark oil ring which is hard to discern in the figure, owing to its dark background, but is easily visible in the original photomicrograph. Interpretation of Figure 2d is uncertain, but it may represent a microemulsion of brine ("holes") and organic material (light colored matrix). The encapsulation of the particle by dark oil is reminiscent of Figure 1b.

Brine Composition

Table 1 compares brine content and composition for sludge as a function of depth in two BM caverns. For both caverns, the proportion of brine in sludge increases with decreasing interfacial distance (Δ feet), while the brine salinity and strontium ion concentrations decrease. These opposing trends may largely be explained on the basis of probable introduction of fresh or brackish water, used in cavern operations, into the sludge layer. The introduced water increases the overall water/brine content of sludge but dilutes the inorganic constituents relative to the original sludge-entrained brine. The effect of introduced water on bromide and sulfate concentrations as well as isotopic D and ^{18}O composition depends on their degree of similarity in the original brine versus introduced water.

For both caverns, the composition of sludge-entrained brine is markedly different than the bulk brine below the sludge layer. Their general dissimilarity clearly indicates a separate origin for the two types of brine. While bulk brine is derived from solution mining of the cavern, sludge-entrained brine is derived from settling of oilfield brine present at low levels (ca 0.02-0.04 wt%) in crudes used to fill the cavern. The relatively high Sr(II) levels observed, particularly at interfacial distances where intrusion of fresh water is low, is typical of oilfield brine.[6]
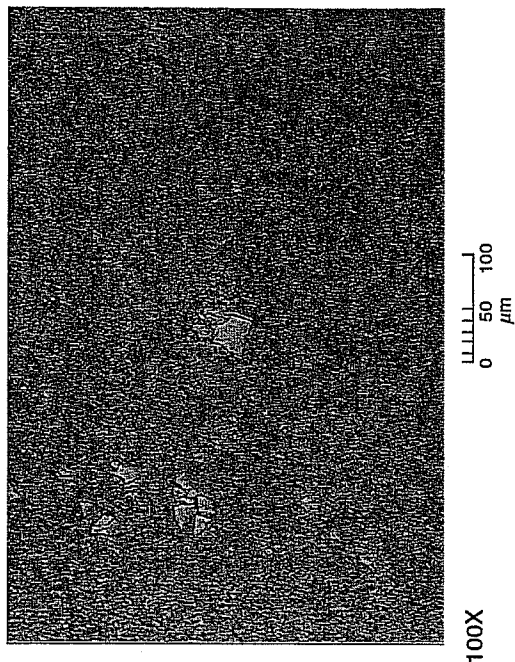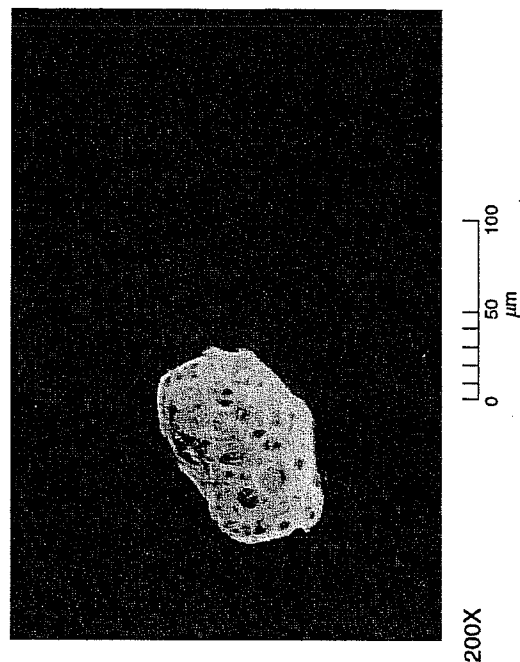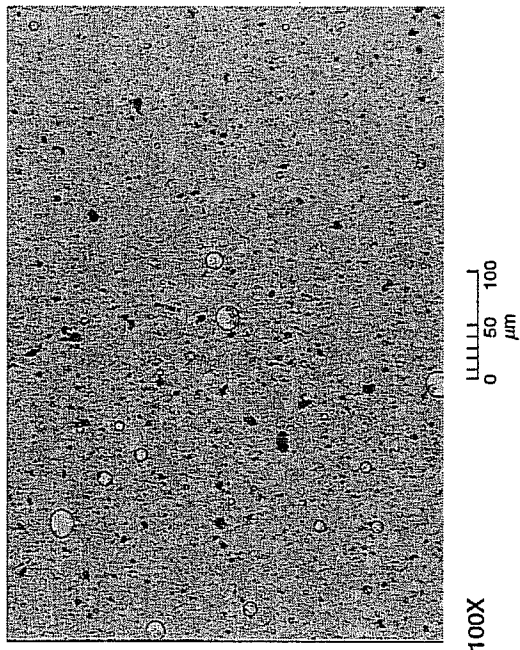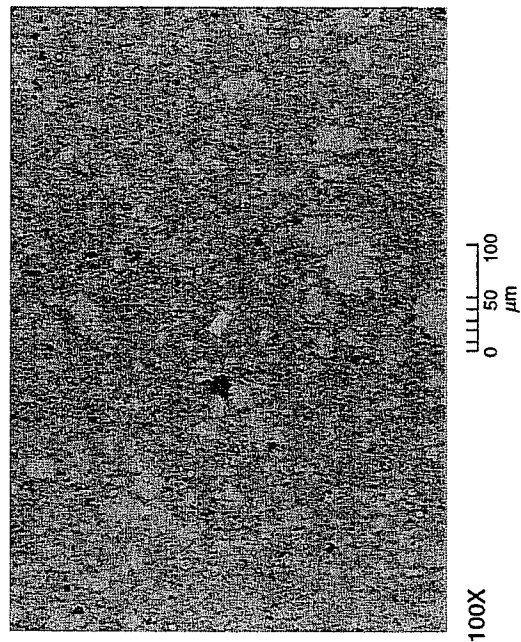
Figure 2.   Photomicrographs of Selected Sludges.   (a,b) are Centrifuged
BM102 Sludges, (b) was Spiked with 100 ppm Poly(ethylene
glycol) Prior to Ultracentrifugation.   (c) Shows Mineral Matter
in WH102 Sludge.   (d) Shows an Unusual Particle in BM102
Sludge.

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Table 1. - Properties and composition of sludge-entrained versus bulk brine in two Bryan Mound Caverns

Cavern	Δ Feet	Sludge Composition, Wt%		Brine Specific Gravity (60/60° F)	Brine Composition, Wt%					Stable Isotope Ratios	
		Water	Brine		Water	NaCl	Br⁻	$SO_4^=$	Sr^{2+}	δD	$δ^{18}O$
BM105	13	6.7	9.1	1.1940	73.9	25.7	0.036	0.39	0.0117	-15	+1.0
	11	7.5	9.9	1.1790	75.9	23.7	0.037	0.40	0.0124	-19	+1.0
	8	14.0	17.2	1.1344	81.6	17.9	0.033	0.43	-	-13	+1.0
	5	19.8	24.1	1.1315	82.1	17.5	0.030	0.37	0.0085	-20	+0.1
	1	28.4	31.4	1.0698	90.4	9.4	0.014	0.23	0.0064	-21	-0.7
	0	42.4	47.1	1.0713	90.1	9.6	0.013	0.26	0.0052	-19	-1.0
	-1	-	-	1.2058	72.6	27.2	0.004	0.19	0.0006	-22	-1.4
BM108	5	2.9	4.1	1.2233	71.0	29.0	0.040	0.43	0.0152	-24	-0.7
	4	3.0	3.9	1.1787	76.5	23.5	0.044	0.45	0.0152	-30	+0.1
	1	9.8	12.0	1.1339	81.7	17.8	0.037	0.45	0.0108	-21	+1.6
	0	11.0	13.3	1.1296	82.8	17.2	0.034	0.44	0.0105	-14	+2.1
	-3	-	-	1.2063	72.5	27.3	0.011	0.20	0.0007	-16	-1.3

The results also indicate very little vertical mixing of brine within sludge. A particularly striking example is the three-fold difference in salt content and greater than ten-fold difference in Sr(II) content in sludge-entrained versus bulk brine at the actual interface in cavern BM105. However, significant differences occur in average brine compositions over distances as little as one foot throughout the sludge layer in both caverns. Based on the photomicrographs shown earlier it is likely that little intermixing actually occurs even between more or less adjacent brine droplets in sludge, because of their isolation in the oil matrix. Therefore, it follows that in cases where average brine properties reflect dilution of original sludge-entrained brine by fresh water, the actual situation may be coexistence of droplets of unadulterated oilfield brine intermingled with those of fresh water rather than formation of droplets of uniform, average composition.

The discovery that sludge-entrained brine was derived from settling of oilfield brines present in crude oil added to caverns, rather than some type of incorporation of bulk brine left over from solution mining, was a major milestone in this research project because it clearly indicated settling to be the primary mechanism for sludge formation. The vertical stratification of sludge serves as additional evidence for its formation through a depositional process.

Table 2 lists specific gravity, pH and acid numbers for sludge-entrained and bulk brines from selected caverns. The wide range of specific gravities for sludge-entrained brine reflects varying levels of fresh water intrusion, whereas the consistently high (near 1.2) bulk brine data reflect approximately saturated salt levels in all cases. The pH of sludge-entrained brine typically varies between 6 and 7; the pH of bulk brine generally occurs in the range between 5 and 6. As footnoted in the table, the exceptionally low pH's of brines from Bayou Choctaw (BC) Cavern 15 resulted from the significant concentrations of acetic and propionic acids in those samples. By comparison, the concentration of acetic plus higher carboxylic acids in most other brines tested was a negligible (<2%) proportion of the total acidity determined by titration with KOH (ASTM D664).

Although the total acid contents of bulk brines were uniformly low (0.7-1.4 mg KOH/g), total acidity for sludge-entrained brine ranged anywhere from 2 to 10 times the levels found in bulk brine. (Besides the results listed in Table 2, acid numbers up to an estimated level of 17 mg KOH/g were reported earlier in Sections 1A and 1B[1,2]). The lack of apparent correlation between pH and acid number for either type of brine indicates that the material(s) titrated in the acid number determination are weakly acidic. Also, the low total and organic carbon contents (typically <0.1 wt%) of brines (except for the BC15 samples) precludes significant contribution of organic acids or bicarbonate to total acid number in most cases.

Table 2. - Properties of bulk versus sludge-entrained brine from selected caverns

Cavern	Sample No.	Type[a]	Specific gravity (60°F)	pH	Acid No. (mg KOH/g)[b]
WH117	90SPR112	S	1.0186	7.19	1.52
	90SPR114	B	1.2051	5.50	0.94
WH114	87SPR027	S	1.0313	6.95	1.58
	87SPR028	B	1.2051	5.80	0.78
BM113	90SPR049	S	1.2057	5.89	3.09
	90SPR050	B	1.2055	5.04	1.24
BM104	87SPR011	S	1.1651	—	3.62
	87SPR012	B	1.2044	6.66	1.25
WH110	89SPR263	S	1.0918	6.94	3.63
	89SPR264	B	1.2047	5.07	0.68
WH107	90SPR183	S	1.0958	7.00	4.82
	90SPR184	B	1.1633	5.83	0.69
BM101	89SPR174	S	1.1148	5.74	5.13
	89SPR175	B	1.1785	6.32	2.07
WH103	89SPR038	S	1.0788	7.10	5.56
	89SPR041	B	1.2057	6.78	1.14
BC15	89SPR289	S	1.0363	3.80	6.15[c]
	89SPR291	B	1.1946	4.29	0.46[d]
BM102	90SPR022	S	1.0773	6.41	6.80
	90SPR023	B	1.2055	5.82	1.41

[a]S = sludge-entrained, B = bulk.
[b]Via ASTM D664.
[c]Contribution of acetic + propanoic acids to acid no. = 0.86 or 14%.
[d]Contribution of acetic + propanoic acids to acid no. = 0.34 or 74%.

Table 3 lists concentrations of selected metals capable of reaction with KOH under conditions of the D664 procedure (solvent = 0.5% water, balance 1:1 toluene: isopropanol; titrant = 0.1 N KOH in isopropanol). Acid numbers were calculated from the indicated concentrations of Mg(II) assuming stoichiometric formation of $Mg(OH)_2$ at the equivalence point of the titration. Relative to Mg, the concentrations of the other elements were negligible; thus, they were neglected in the acid number calculation. For comparison, measured acid numbers are also shown in the table.

Agreement between calculated versus measured acid numbers was sufficient to conclude that acid numbers for sludge-entrained or bulk brines largely reflect Mg(II) concentrations, except in the relatively rare cases where significant levels of acetic and propanoic acids are present (e.g. BC15). In addition, the synthetic $MgCl_2$ solution yielded an acid number commensurate with the level of Mg(II) present. It follows that the higher acid numbers for sludge-entrained versus bulk brines typical of Table 2 simply indicate higher Mg(II) levels for the oilfield-derived brine in sludge versus the bulk brine obtained from solution mining of salt caverns. The range of Mg concentrations reported in Table 3 and implied by acid numbers in Table 2 is typical of oilfield brines.[6] Since acid numbers for whole sludge largely reflect that of the entrained brine (see Sections 1A and 1B[1,2]), the higher acid numbers obtained for sludge versus bulk crude from most caverns simply reflect Mg(II) present in the entrained brine. Thus, sludge acid numbers have no general significance or usefulness as indicators of contamination or microbial activity.

The organic constituents of sludge-entrained brines typically fall within the following groups: acetic and propanoic acids (as noted above), higher carboxylic acid homologs (up to C_{20}), phenol and lower alkylphenol homologs, sulfoxides (especially in caverns where sour crudes were stored), basic nitrogen compounds (e.g. alkylquinolines), and various types of monomeric and polymeric glycols. The distribution of individual members within each group, the overall breakdown among groups, and the total organic carbon contents of sludge-entrained brines often varied significantly from cavern to cavern and even as a function of interfacial distance within a given cavern. Analysis of organic sludge-entrained brine constituents has been described in detail in a separate report;[5] the organic composition of bulk brines was not investigated.

As an illustration of the analytical methodology, Figure 3 shows a total ion current GC/MS chromatogram of organics present in a sludge-entrained brine taken at the interface (Δ feet = 0) of cavern BC15, noted in Table 2 to contain relatively high levels of acetic and propanoic acids. In this sample, the distribution of carboxylic acids diminishes rapidly with carbon number ($\geq C_6$ were in low abundance, except for C_{16} and C_{18} as indicated). The dominant components present are propylene glycols with degrees of polymerization (n) ranging from 1-4 [$HO(CH_2CH(CH_3)O)_nH$].

Table 3. - Trace metal content versus acid number for selected brines

Cavern	Interfacial Distance (Δfeet)	Sample No.	Metal Concentration (ppm)						Acid Number (mg KOH/g)	
			V	Pb	Cr	Al	Fe	Mg	Measured	Calculated from Mg Content
WH102	0	89SPR023	0.24	<0.2	0.13	0.21	0.16	1830	8.48	8.45
BM105	8	87SPR109	0.27	<0.2	0.15	0.52	4.01	2560	11.0	11.8
BM105	1	87SPR111	0.19	<0.2	0.10	0.23	2.88	1060	5.54	4.89
BM105	0	87SPR112	0.22	<0.2	0.08	0.52	6.40	920	nd	4.25
BM105	-1[a]	87SPR113	0.40	<0.2	0.13	0.39	<0.08	280	1.34	1.29
—	—	Saturated NaCl[b]	nd[c]	nd	nd	nd	nd	nd	0.06	<0.1
—	—	Saturated NaCl spiked with 1.75 mg/g Mg(II)[b,d]	nd	nd	nd	nd	nd	(1750)	7.93	8.08

[a]Bulk brine.
[b]Synthetic solution (not from a cavern).
[c]Not determined.
[d]Added as $MgCl_2.6H_2O$.

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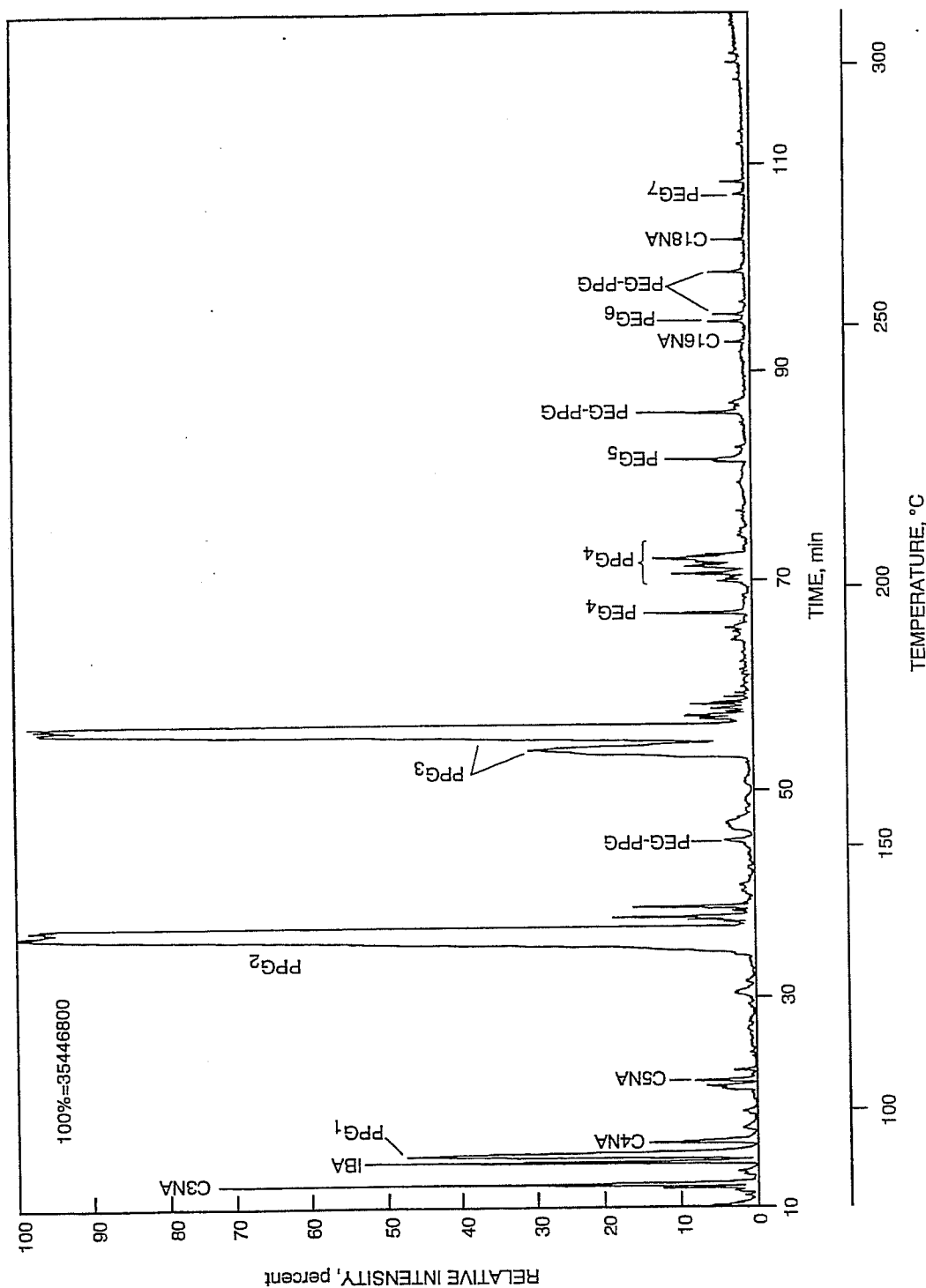**Figure 3.** GC/MS Total Ion Current Chromatogram of Organics Extracted from Brine in BC15 Sludge (Δfeet = 0). Straight Chain Carboxylic Acids are Designated CXNA, Where X = Carbon Number. Poly(propylene glycol) Homologs are Designated PPG_n, Where n = Degree of Polymerization. Poly(ethylene glycol) Homologs are Designated PEG_n. PEG-PPG = PEG/PPG Copolymer. IBA = Isobutyric Acid.

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The balance of the organics consists of small quantities of other polyglycol types and other minor unidentified components. The indicated prevalence of glycols over other compound types is fairly typical of the brines examined.

Stabilization of Brine in Sludge

NMR studies of reconstituted sludge-entrained brines, where H_2O had been replaced with D_2O (see Experimental), provided some insight into the degree of oil-water interactions in sludge. The relaxation rate $(1/T_1)$ determined is a measure of how quickly the bulk D_2O magnetic moment recovers after being disturbed by an NMR pulse. This rate is determined by the average chemical environment, or degree of structuring, of D_2O within the sample as well as by temperature. Because relaxation mechanisms are less efficient in cases where D_2O motion is uninhibited, $1/T_1$ decreases with increasing temperature and decreasing D_2O structure, and vice versa.

Figure 4 shows the temperature dependence of relaxation rate of centrifuged WH112 sludge (sample No. 87SPR126) as a function of brine content. The initial centrifuged sludge contained approximately 2% D_2O; the incremental increases in D_2O concentration via addition of reconstituted brine are noted in the figure. The D_2O relaxation rate of the neat centrifuged sludge is well above that of pure D_2O at all temperatures, but the difference becomes greater at higher temperatures (lower $1/°K$). As more brine is added, the resulting relaxation rate approaches that of pure D_2O, in accordance with the expected decrease in D_2O structure as the mole fraction of brine in sludge increases.

The combination of NMR data and previously discussed microscopic examinations of centrifuged sludge indicates a significant degree of dispersion and structure in the remaining brine. To investigate the possibility of micellar structures in sludge, an additional series of NMR experiments was carried out to compare D_2O relaxation in sludge versus synthetic micellar systems. In each synthetic system, the ratio of surfactant to oil was kept constant and the proportion of D_2O was varied. Aerosol-OT (dioctylsulfosuccinate) was used as the surfactant; various solvents were employed as "oils".

Figure 5 shows results for the synthetic micellar systems and sludge obtained at 20°C. The system with the highest proportion of surfactant (4.75/1 molar ratio of isooctane/A-OT) showed a pronounced increase in relaxation rate with decreasing D_2O content. The other two systems with similar proportions of surfactant (35/1 of isooctane/A-OT and 31.2/1 of (75/25 decane/benzene)/A-OT) exhibited equivalent moderate increases in relaxation rate until the mole fraction of D_2O fell below 0.3; at lower D_2O mole fractions, a sharp rise in relaxation rate was observed. The sludge
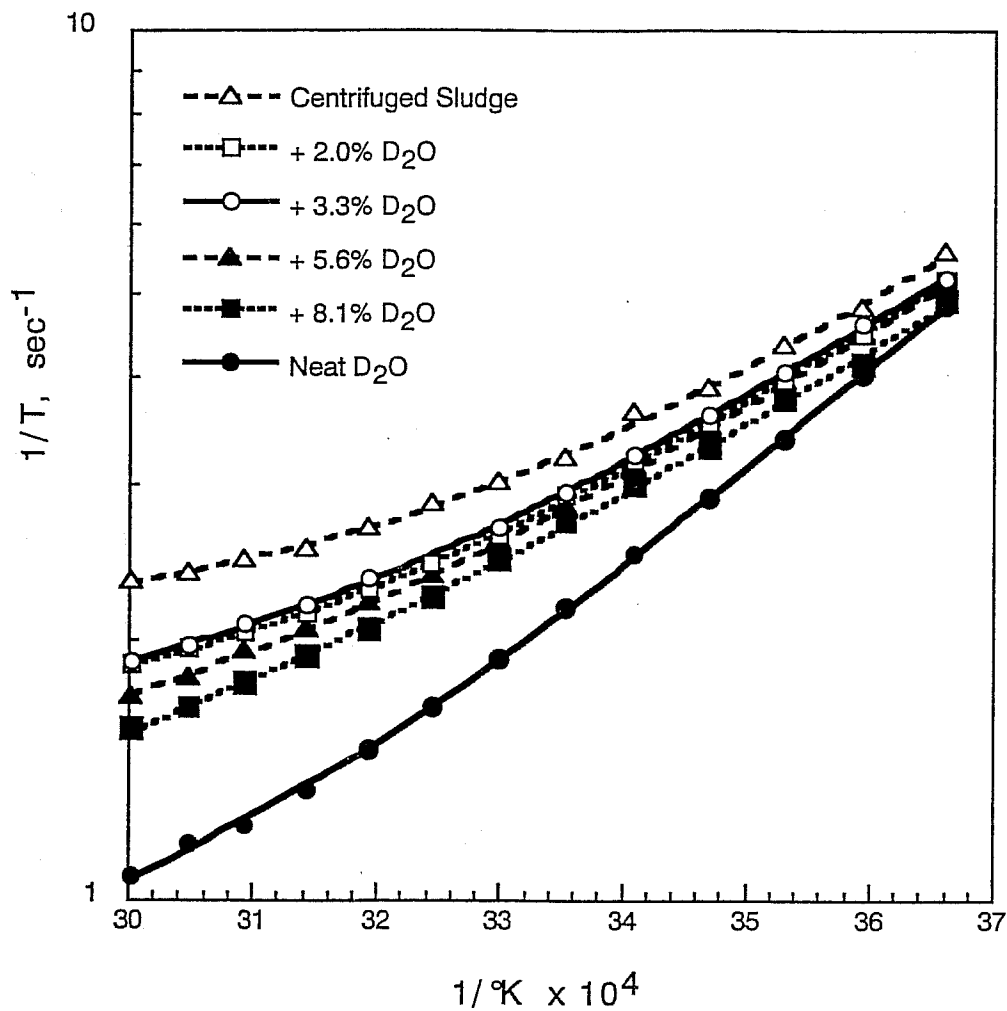
Figure 4. Temperature Dependence (1/°K) of Relaxation Rate (1/T$_1$) Determined by NMR for centrifuged WH112 Sludge (2% D$_2$O) with Various Levels of Additional D$_2$O from Incremental Spiking with Reconstituted Brine.
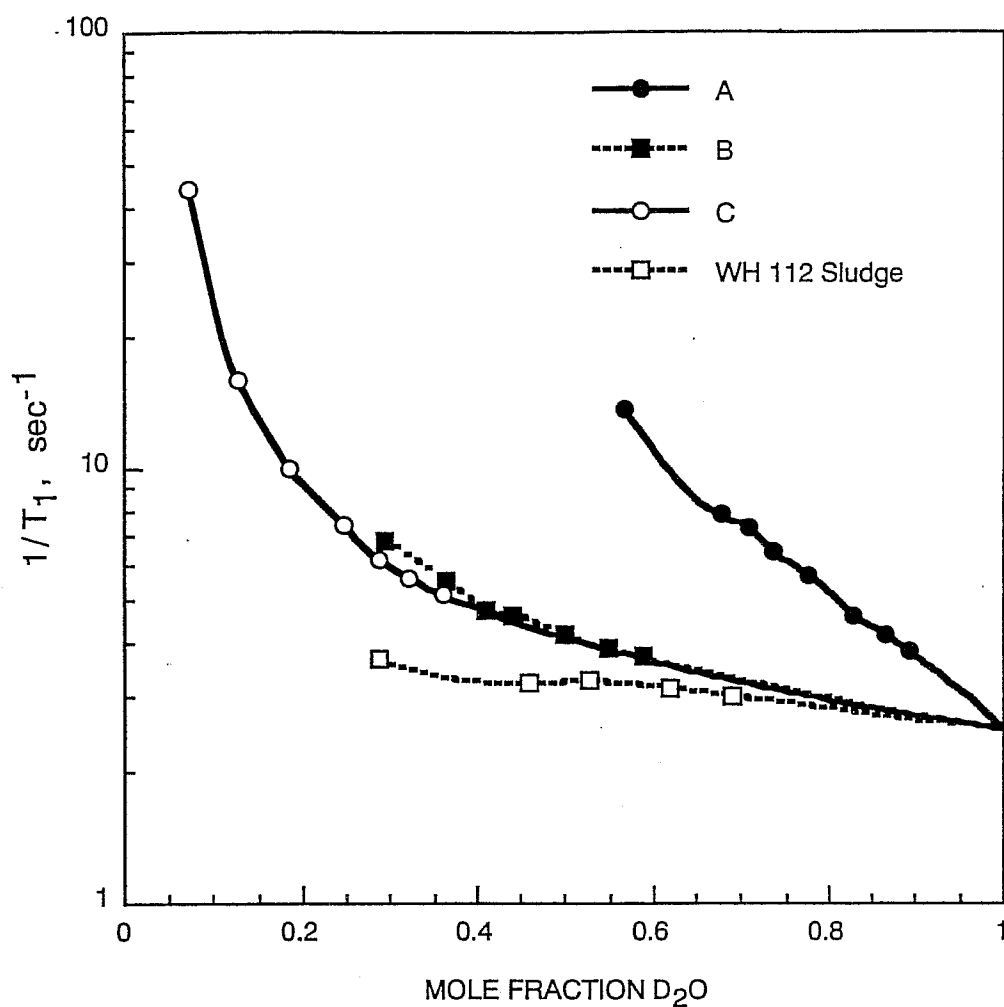
Figure 5. NMR Relaxation Rate $(1/T_1)$ as a Function of D_2O Mole Fraction for WH112 Sludge and Synthetic Surfactant/Solvent/ D_2O Mixtures. A = 4.75/1 Isooctane /A-OT, B = 35/1 Isooctane/A-OT, C = 31.2/1 (75/25 Decane/benzene)/A-OT.

exhibited a modest increase in relaxation rate; points below 0.3 mole fraction D_2O could not be obtained because that level of D_2O corresponded to the limit of brine removal attainable by ultracentrifugation, even for extended time periods of up to 12 hours.

Interpretation of Figure 5 was complicated by the lack of sludge data below 0.3 mole fraction D_2O and the difficulty in estimating an appropriate oil/surfactant ratio. A significant increase in relaxation rate at low D_2O molar ratios would have confirmed presence of micelles. An estimate of oil/surfactant ratio based on total carbon content of sludge-brine from Cavern WH102, corrected for carbon contributed by acetic and propanoic acids, yielded a result of 10,000. This estimate was based on the assumptions that all brine-soluble organics (except for acetic and propanoic acids) behaved as surfactants, that all available surfactants were contained in the brine phase, and that the oil and surfactants had the same average molecular weight. In spite of the very approximate nature of the estimate, it nevertheless points to a very large oil/surfactant ratio, which is consistent with the relationship of sludge versus model surfactant curves in Figure 5, and presence of at most a small proportion of sludge brine in micellar systems. Potentially, the generally small proportion of brine not removed by ultracentrifugation of a given sludge may correspond to that present in micellar or similar chemically stabilized systems.

Results from experiments conducted to determine effects of pH adjustment and dilution of sludge by organic solvents or water on degree of brine removal by ultracentrifugation varied greatly among the various sludges examined. Figure 6 compares brine recovery (wt% whole sludge) as a function of centrifuge speed (rpm) from as-received sludge from cavern BM105 to aliquots of the same sludge spiked with 0.06 wt% HCl, 2.5 wt% NaOH, and 12.5 wt% deionized water. For neat sludge, brine removal increased linearly with centrifuge speed to a maximum of 17 wt% at 17,000 rpm. Brine removal from HCl-or NaOH-spiked sludge was appreciably lower, and nearly independent of centrifuge speed. Results for water-spiked sludge are plotted twice; both the proportion of the original brine removed (corrected for dilution by added water) and total brine removed (raw data) are indicated in the figure. The effect of adding water to this sludge on brine removal was minimal.

Figure 7 shows results analogous to those in Figure 6 for a sludge from a different cavern, WH112. This sludge sample was the same one used in the NMR experiments (87SPR126). In contrast to the BM105 sludge, any alteration of the composition of this sludge led to increased brine removal over that obtained from the neat sludge.

Figures 8 and 9 show ultracentrifugation results obtained with two additional sludges from caverns WH103 and WH104. Results for HCl-treated sludge deviated the most from those for neat sludge in both figures.
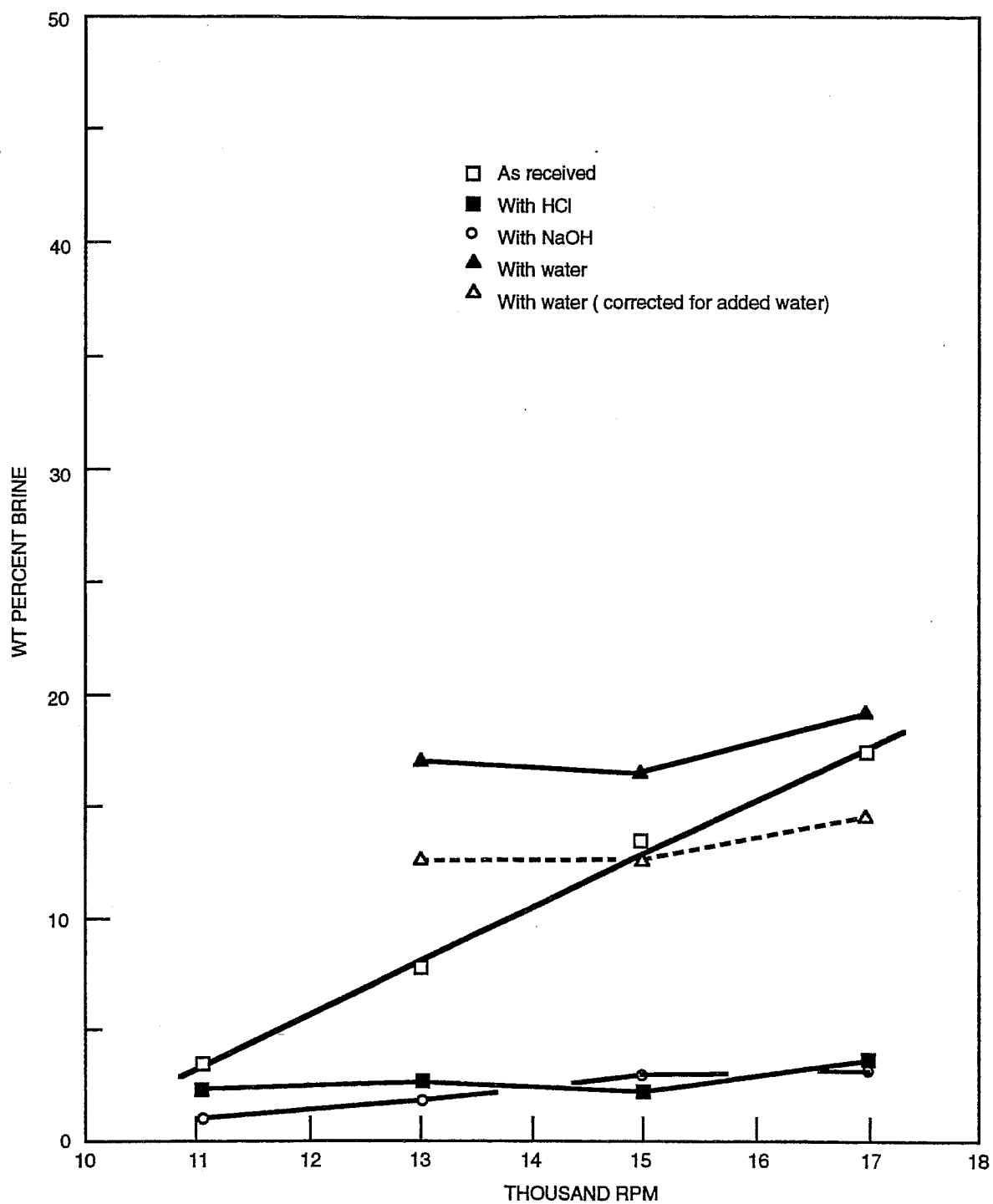
Figure 6. Recovery of Brine as a Function of Centrifuge Speed (rpm) from BM105 (Δfeet = 1) sludge.
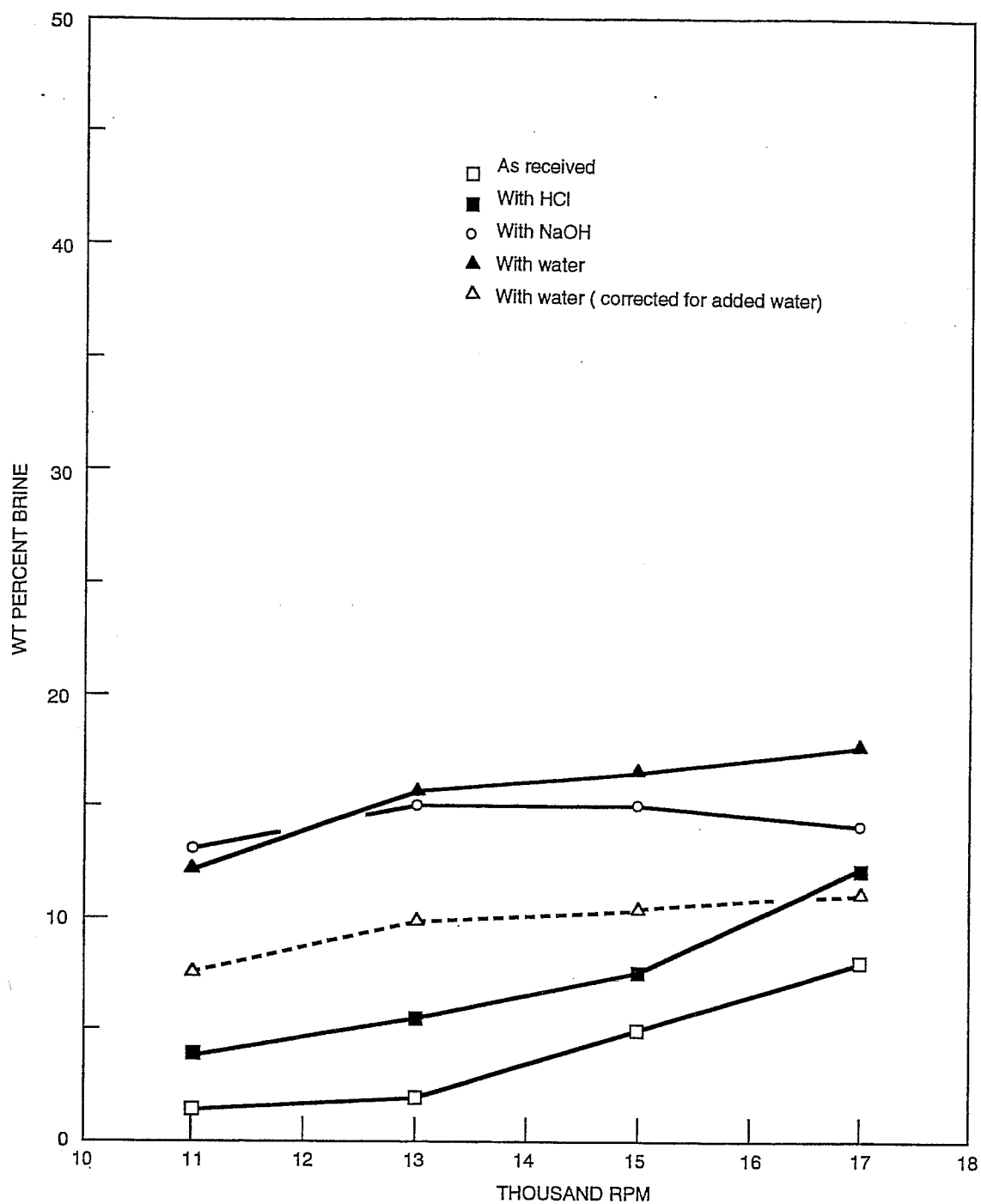
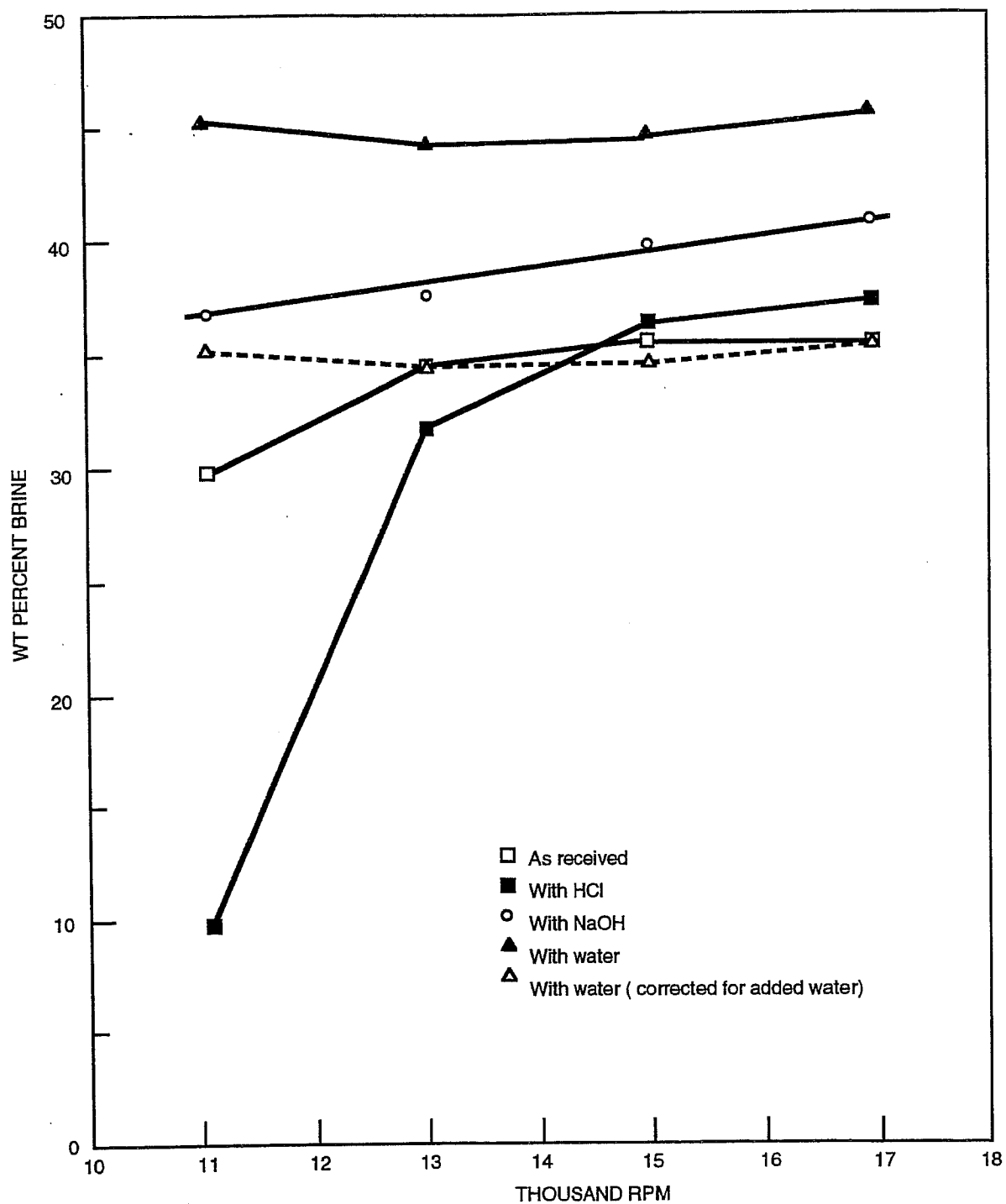**Figure 7.** Recovery of Brine as a Function of Centrifuge Speed (rpm) from WH112 (87SPR126) Sludge.

Figure 8. Recovery of Brine as a Function of Centrifuge Speed (rpm) from WH103 Sludge.
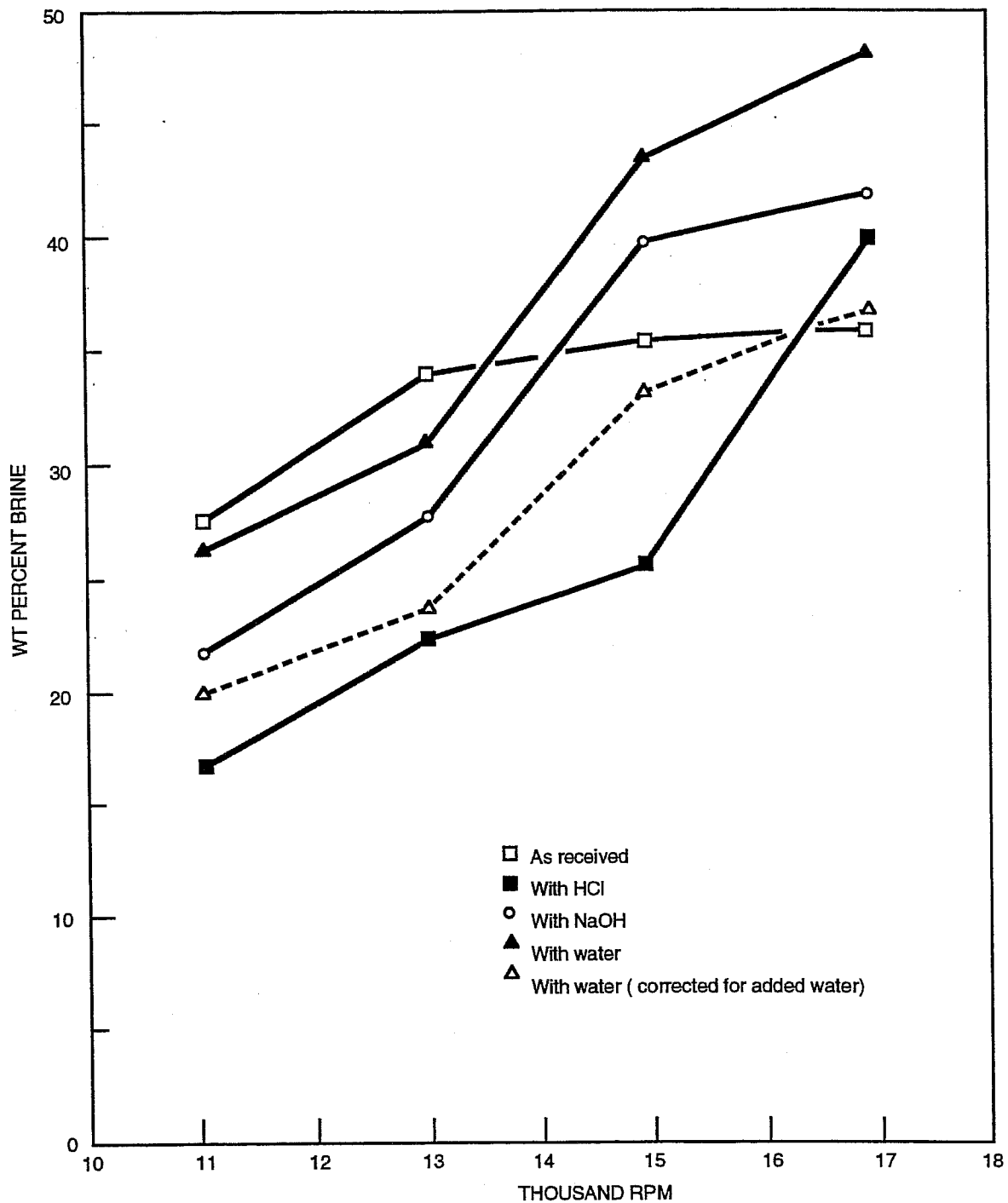
Figure 9. Recovery of Brine as a Function of Centrifuge Speed (rpm) from WH104 Sludge.

Dispersal of brine in sludge could be stabilized by any of a number of forces. For example, electrostatic repulsion of brine droplets via formation of localized charges from brine electrolyte components near the droplet surface is one possibility. Stabilization of colloidal suspensions of clay and other inorganic particles in water occurs via this type of mechanism. However, the typically minimal effect from dilution of sludge with deionized water on brine recovery via centrifugation (except for W112 sludge, Figure 7) casts doubt on the importance of dispersion mechanisms based on brine electrolytes.

Alternately, brine droplets could be stabilized through interactions with polar compounds in the surrounding oil. This hypothesis is supported by the observed increase in brine stabilization for some sludges from addition of HCl or NaOH. Addition of strong acid or base would respectively result in ionization of basic and acidic compounds in the oil. The ionized organics would subsequently promote brine dispersal by acting as surfactants. Significant surfactant properties for selected types of polar compounds in crude oil, notably carboxylic acids, have been reported.[7] Thus, the variable degree of stabilization observed in Figures 6-9 for HCl-and NaOH-spiked sludges may reflect the various proportions of acids and bases present in the crude oil components of each sludge. Destabilization by HCl/NaOH addition, as observed in some cases, could result from neutralization of species providing stabilization in the neat sludge.

Simple physical entrapment of brine resulting from presence of waxes and other viscous or solid components is another potential explanation for brine dispersal. In order to evaluate this hypothesis, three aliquots of a BM105 sludge were spiked with 10 wt% heptane, cyclohexane, and toluene and then centrifuged. Addition of any of the solvents noticeably reduced the viscosity of the sludge. The BM105 sludge used in these experiments was sampled at the same time as the one shown earlier in Figure 6, but was obtained at a greater interfacial distance (Δ feet = 5 instead of 1). Since this sludge was similar, but not identical, to the one employed earlier, the previously conducted centrifuge tests on neat versus HCl-spiked samples were repeated using the new material. For comparison to the HCl-spiked sludge, a separate series of centrifugation tests was also conducted on aliquots spiked with 1 wt% 1-methyl-1-cyclohexanecarboxylic acid.

Results from ultracentrifugation of the BM105 (Δ feet = 5) sludge are shown in Table 4. Brine recoveries from neat samples of this sludge were appreciably lower than obtained from the BM105 (Δ feet = 1) sludge (Figure 6), even after taking into account differences in their total brine content (Table 1). However, HCl spiking resulted in comparable degrees of stabilization in the two sludges. Although solvent dilution of sludge resulted in a minimal increase in brine recovery at 15,000 rpm, the proportion of brine recovered at 17,000 rpm was substantially less than that for neat sludge in each case. Thus, the hypothesis of physical entrapment of brine in sludge via viscosity effects was effectively refuted by these results.

Table 4. - **Brine recovery from centrifuging BM105 sludge (87SPR110) with various additives**

Centrifuge Speed (thousand rpm)[a]	Compound Added		Brine Recovered
	Name	wt%	(wt%)
17	None	—	4.9
15	(as received)		0.0
17	HCl	0.06	0.7
15			0.2
17	Heptane	10.0	1.3
15			0.6
17	Cyclohexane	10.0	1.6
15			1.0
17	Toluene	10.0	2.6
15			1.8
17	1-methyl-1-	1.0	8.3
15	cyclohexanecarboxylic acid		0.7

[a]Recovery of brine from all samples was negligible at centrifuge speeds below 15,000 rpm.

The enhanced recovery of brine from the samples spiked with the carboxylic acid was particularly interesting. Potentially, dissolution of the acid in brine decreased the lipophobic nature of the brine droplets, thereby facilitating their coagulation via migration through the oil phase and subsequent separation via centrifugation. Thus, one possible mechanism for stabilization of sludge via HCl addition might be protonation of carboxylic acids dissolved in brine, resulting in their subsequent partitioning back into the oil phase. The resulting level of organics in the brine would be lower, thereby making the droplets more lipophobic and less able to migrate and coalesce within the oil phase. This interpretation is contradictory to the one advanced earlier proposing surfactant formation from oil-derived polar compounds via HCl or NaOH addition, but fits the existing data at least as well.

The mechanism(s) responsible for stabilization of brine in sludge are still largely open to speculation. However, the available evidence points to chemical, rather than physical phenomona. The above cited failure of solvent dilution of sludge to promote brine separation via ultracentrifugation as well as additional experiments in reconstitution of sludge from its components largely rule out simple physical entrapment of brine in sludge. Sludge reconstitution consisted of a brief series of experiments in which sludge was distilled into light and heavy fractions and the heavy fraction was further separated into waxes, oils, and asphaltenes. Various fractions were then combined, mixed, and the resulting mixtures were examined under a

microscope. In the course of the work, it was found that addition of the light distillate fraction was actually necessary to form an emulsion resembling that of the original sludge.

Although some of the D_2O structure evident from the NMR experiments undoubtedly resulted from the high concentration of inorganic salts present, it is likely that the balance results from oil-water interactions. In addition, the observed inability of ultracentrifugation to remove brine below a given level, plus the largely submicroscopic size of brine droplets in centrifuged sludge supports the existence of at least minor proportions of brine in highly dispersed, chemically stabilized states.

However, the major proportion of brine in sludge, that which is removed by ultracentrifugation and easily seen under a microscope, is clearly not micellar or analogous forms. Based on the various degree of brine stabilization for sludges in Figures 6-9 from HCl and/or NaOH treatment, stabilization of the major proportion of brine occurs through chemical means, but via unknown mechanisms. The available evidence indicates that the organic constituents of brine probably impact its dispersion to a much greater extent than inorganic solutes.

SUMMARY AND CONCLUSIONS

Sludge-entrained brine is clearly derived via settling of brine present in as-received crude oil shipments placed into storage. Incorporation of bulk brine into sludge is nonexistent or at most insignificant. However, some intrusion of fresh or brackish water used in cavern operations into the sludge layer does occur. This intrusion reduces the average salinity and concentrations of inorganic ions present in the original sludge-entrained brine and increases the total volume of the aqueous phase.

The size of brine droplets in sludge ranges from approximately 30 μm in diameter down to submicroscopic (<1μm). The size distribution may reflect that of brine in as-received crude or it might reflect varying degrees of agglomeration during settling. Some of the intermediate size droplets appear to be encapsulated with a thin layer of dark organic material which may indicate brine interaction with high boiling oil-derived compounds containing hydrophilic groups. The very small sized droplets appear to be in some type of chemically dispersed, possibly micellar, state.

Sludge-entrained brine contains inorganic ions common to oilfield waters, including Sr. The high acid number of sludge brine is derived from its significant Mg(II) content. It also contains low levels of hydrophilic organic components derived from crude oil--including carboxylic acids, sulfoxides, phenolic compounds and nitrogen compounds -- as well as synthetic polyglycols used as demulsifying or drying agents. Some of these organic constituents probably aid in stabilization of brine in sludge.

Overall, stabilization of brine in sludge appears to occur via chemical means rather than simply via physical entrapment via waxes or other viscous oil-derived components.

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